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Thermodynamic properties for the heterogeneously catalyzed selective oxidation of cyclohexane in carbon dioxide expanded media by experiment and simulation

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Synopsis

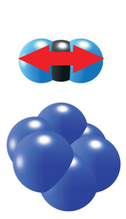
The development of novel octahedral molecular sieves is of particular interest for the catalytic oxidation of cyclohexane in carbon dioxide expanded media. In this project, the thermodynamic properties of the relevant mixtures are investigated. Therefore, the mixtures of interest are studied with respect to the gas solubility both by experiment and molecular simulation.

A literature survey shows a lack of gas solubility data for carbon dioxide and especially oxygen. In a first step, the Henry's law constant of carbon dioxide in pure cyclohexane and in pure cyclohexanone as well as in mixtures of these components is measured between 298 and 393 K. That study is then extended to the gas solubility of oxygen. A synthetic method is used for the experiments.

Molecular simulations are performed with multi-center Lennard-Jones models with superimposed electrostatic sites. For some of the components of interest, molecular models are available in the literature [1]. For cyclohexane, cyclohexanol [2] and cyclohexanone new molecular models are developed in this work. Furthermore, a new, improved carbon dioxide model is developed [3]. Unlike interactions are modeled with the modified Lorentz-Berthelot combination rule. The predictions from simulation are compared to experimental Henry's law constant data, which are in a very good agreement. Additionally, high pressure vapor-liquid equilibria of the mixtures are predicted as well as transport properties.

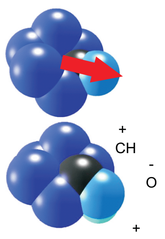
Molecular models developed in this work

The parameters are fitted in the optimization process to yield the correct VLE behavior of the modeled pure substance. The optimization is performed using a Newton scheme as proposed by Stoll [4]. It relies on a least-square minimization of a weighted fitness function that quantifies the deviations of simulation results from a given molecular model compared to experimental data.



Carbon dioxide
3 LJ sites plus point quadrupole

Cyclohexane
6 LJ sites



Cyclohexanone
7 LJ sites plus point dipole

Cyclohexanol
7 LJ sites plus 3 point charges

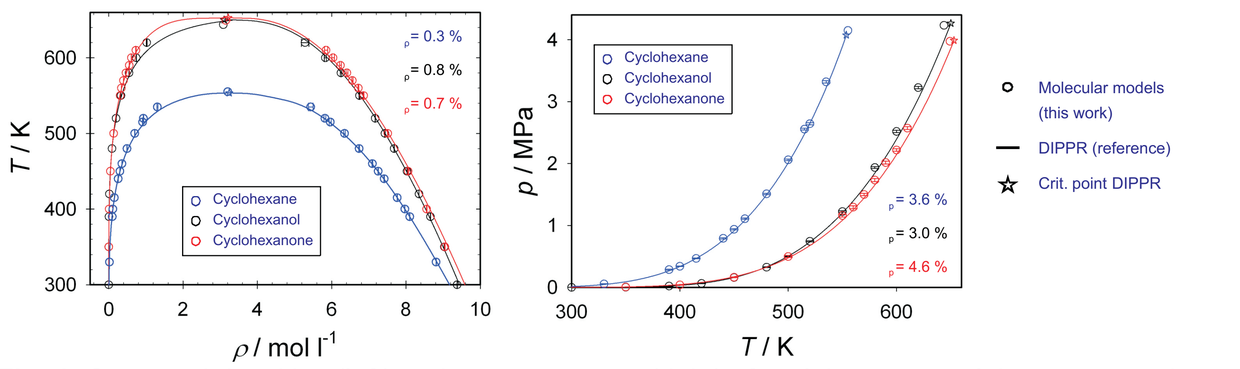


Fig. 1: Saturated densities (left) and vapor pressure (right) of cyclohexane, cyclohexanone and cyclohexanol

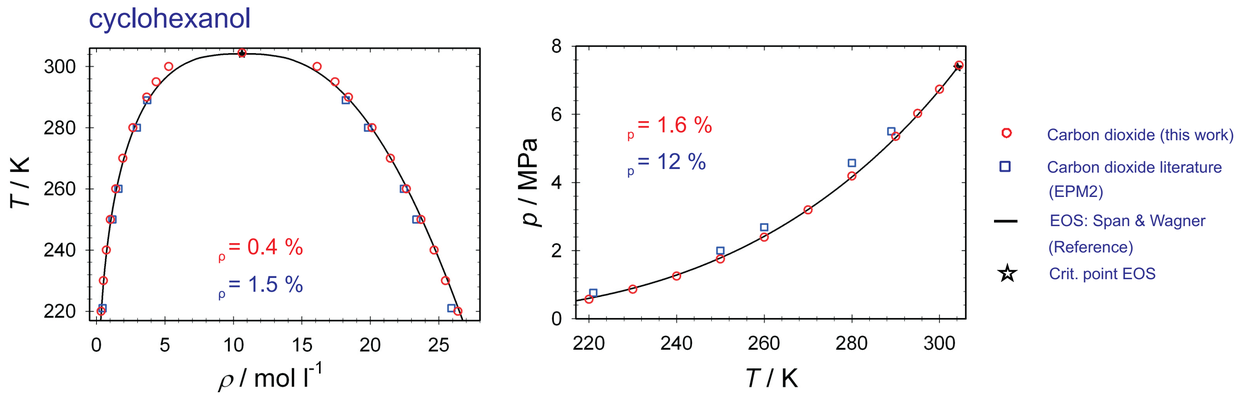


Fig. 2: Saturated densities (left) and vapor pressure (right) of carbon dioxide

Self-diffusion coefficient

Self-diffusion coefficient were obtained by equilibrium molecular dynamics (EMD) simulations following the Green-Kubo formalism. This approach is based on the relationship between the transport coefficients and the time integrals of corresponding autocorrelation functions of microscopic fluxes in a system in equilibrium.

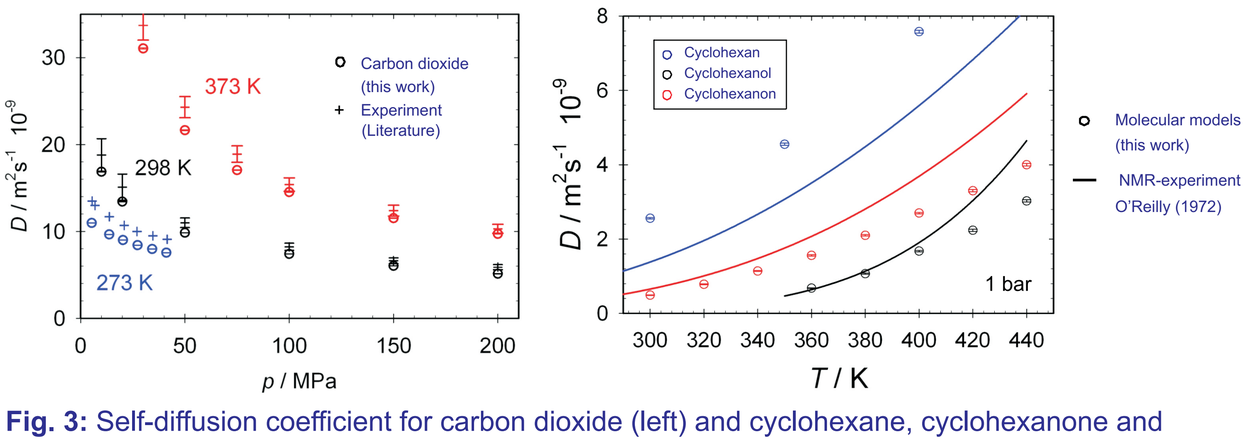
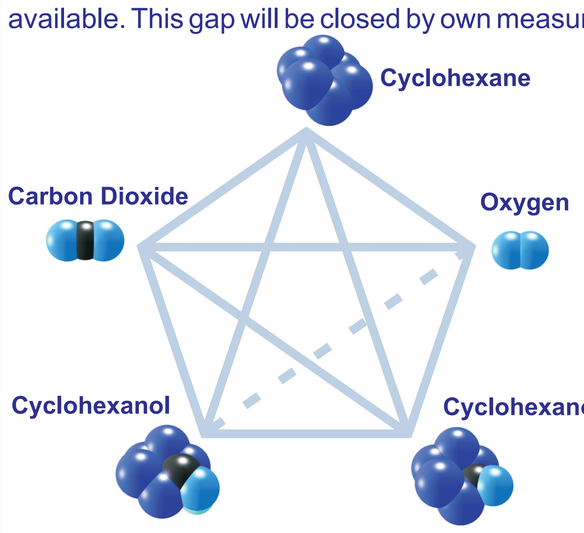


Fig. 3: Self-diffusion coefficient for carbon dioxide (left) and cyclohexane, cyclohexanone and cyclohexanol (right)

Reacting system

Experimental data for binary mixtures, VLE or Henry's law constants, are needed to adjust the unlike interaction parameter ξ. Especially for the subsystem cyclohexanol + oxygen, no experimental data is available. This gap will be closed by own measurements.



Modified Lorentz-Berthelot combination rule

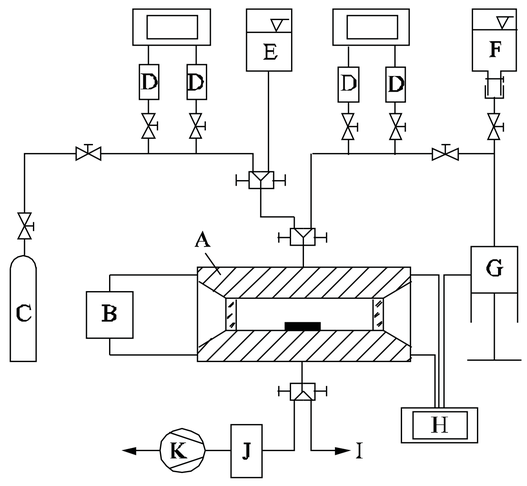
$$\sigma_{AB} = \sigma_A + \sigma_B / 2$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$$

Experimental data available (VLE or Henry's law constants)

Experimental data not available

Gas solubility measurements



A: Cylindrical high-pressure equilibrium view cell with two sapphire windos and magnetic stirrer
B: Thermostat
C: Container for the gas
D: Pressure transducers
E: Tank for rinsing water
F: Tank for solvent mixture
G: High-pressure spindle press
H: AC-brigde with three platinum resistance thermometers
I: Solution outlet
J: Cooling trap
K: Vacuum pump

Fig. 4: Experimental setup

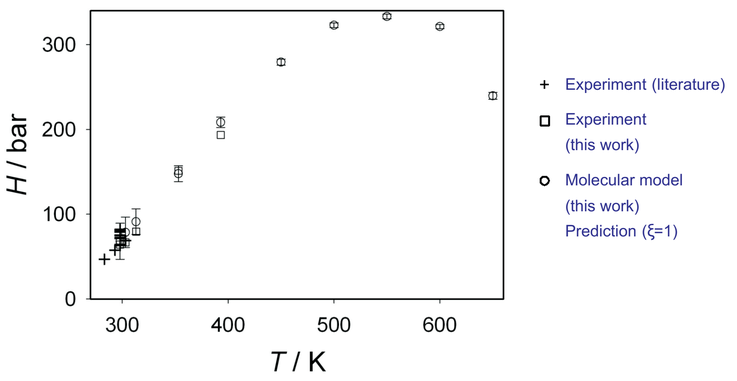


Fig. 5: Henry's law constant of carbon dioxide cyclohexanone

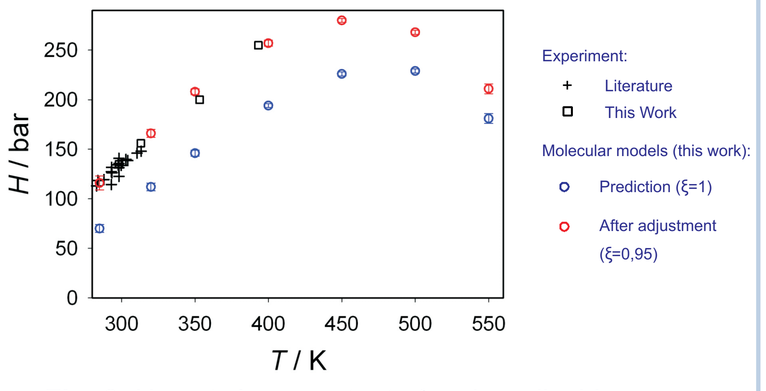


Fig. 6: Henry's law constant of carbon dioxide + cyclohexane

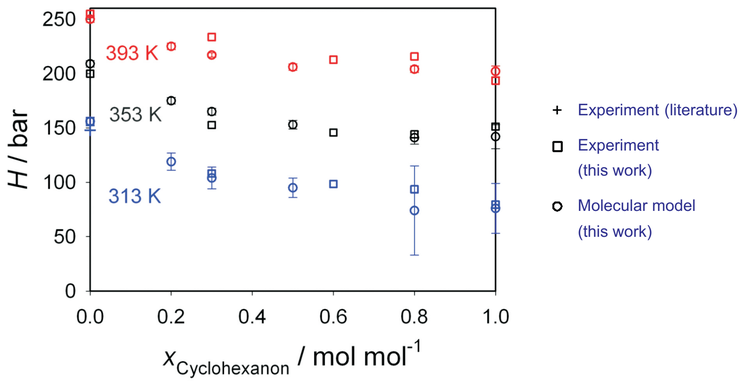


Fig. 7: Henry's law constant of carbon dioxide + cyclohexanone + cyclohexane

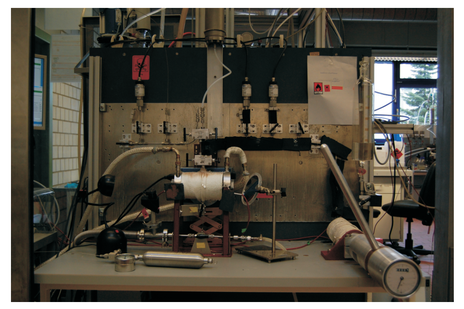


Fig. 8: Gas solubility apparatus

Extrapolation of the experimental Henry's law constant with:

$$H_{CO_2} \lim_{p \; p^s_{liq.}} \frac{f_{CO_2}(T,p)}{x_{CO_2}}$$

$$f_{CO_2} \quad p \; y_{CO_2} \quad {}_{CO_2}$$

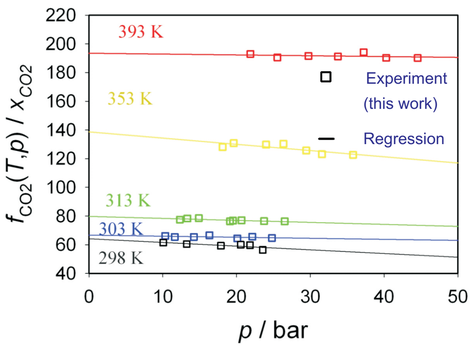


Fig. 9: Plot for determining the Henry's law constant

Literature

[1] Vrabec, J.; Stoll, J.; Hasse, H. J. Phys. Chem. B 105 (2001) 12126-12133.
[2] Merker, T.; Vrabec, J.; Hasse, H. Soft Materials, accepted (2010).
[3] Merker, T.; Engin, C.; Vrabec, J.; Hasse, H. J. Phys. Chem., accepted (2010).
[4] Stoll, J. VDI-Verlag, Düsseldorf (2005), Reihe 3.